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A COLD ELECTRON MASS SPECTROMETRIC ION SOURCE*

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The most widely used method of producing ions from neutral molecules in the ion source of a mass spectrometer or ionization gauge has been electron bombardment. The electron source generally found in mass spectrometers is the thermionic emitter. There are certain difficulties associated with this source arising principally from the unavoidable heating effect of the hot filament. These difficulties can be eliminated by utilizing a cold source of ionizing electrons. Cold electron source devices have been described previously in papers presented at the Eighth Annual ASTM-E-14 Meeting, Atlantic City, New Jersey, and the Eleventh Annual ASTM-E-14 Meeting, San Francisco, California, 1963[7,8]. The results of subsequent investigations into cold electron sources, for mass spectrometric application, form the basis of this report.

The cold electron source chosen for consideration during this phase of the study was the resistance-strip electron multiplier[2,4], activated by electrons from a photocathode or radio-active beta-ray emitting material. This multiplier has previously found application as an ion detector in mass spectrometers and, as such, operates with very low level output currents. For mass spectrometric ionization application, however, the source should be

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capable of producing electron current sufficient to ionize gas molecules.
An additional requirement would be that the device be capable of exposure
to the atmosphere without undue damage. Therefore, this study was designed
to investigate the feasibility of using the resistance strip multipler as
a cold electron mass spectrometric ion source.

The resistance-strip multiplier utilizes electron generation in crossed
electrostatic and magnetic fields. The device possesses one continuous
dynode, as compared to conventional multipliers which use a large number
of individual dynodes. The basic resistance-strip multiplier, shown in
Figure 1, consists of two plane parallel resistive surfaces. These surfaces
are ordinarily made of a semiconducting coating applied to an insulating
base, but may be wholly semiconducting material of the proper volume
resistivity. Equal potential gradients are established along their long
dimensions. The true potential of the field strip is maintained positive
relative to the dynode strip at any given point. Thus the equipotential lines
are parallel to each other and slanted in the direction shown in the figure.
The entire structure is placed in a uniform magnetic field that is normal
to the electrostatic field. An electron released from the dynode strip at
any point will describe a cycloidal path whose initial direction is
determined by the equipotential at its point or origin. It will return to
the dynode strip with an impact energy corresponding to the difference in
potential between its points of origin and impact. In a properly designed
multiplier this energy will be large enough to give a secondary emission ratio
greater than unity. Thus the electron will release more than one electron at
its point of impact. This process, continued along the strip many times,

permits electron current amplification. The total gain in electron current along the strip will be a function of the field strengths and the length of the dynode.

An investigation of several secondary emissive surfaces as possible resistance strip materials, indicated that tin oxide, deposited over a titanium dioxide coated glass strip, was the most suitable material. The tin oxide possessed a high secondary emission yield and was very stable on exposure to the atmosphere when compared to the other films, which included silver-magnesium (Ag-Mg) and beryllium-copper (Be-Cu). Insufficient resistivity of dynode surfaces, when using Be-Cu and Ag-Mg, effectively eliminated these films for resistance strip use. The dynodes were prepared by initially evaporating, in vacuo, a 500 to 1000 Å thick layer of titanium onto a very clean glass strip. The titanium is oxidized in air to a measured resistance in the range of 10 to 20 megohms. Electrical contacts are placed on each end of the strip by evaporating a heavy layer of gold or silver-manganese, employing masks to prevent coverage of the entire strip. Finally a 500 to 1000 Å thick coating of tin is deposited, in vacuo, onto the strip, followed by total oxidation of the tin, in air, at 500° to 600° C. The multiplier field strips were titanium dioxide strips of 50 to 100 megohms resistance.

An electomagnetic multiplier was used to determine the magnetic field strength needed for operation with multiplier dynode voltages of 1000 to 1500 volts. This field strength was found to be between 180 and 200 gauss, for our particular multiplier configuration. Permanent magnet multipliers were assembled based on these findings. The use of permanent magnets greatly reduced the size and weight of the multiplier and eliminated the heating

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effects and power consumption of the electromagnet.

These multipliers were shown to be capable of maximum electron emission currents in excess of 30 microamperes, with operational output currents of 0.5 to 3.0 microamperes. Normal input currents were 1 to 3 nanoamperes, using a photocathode under ultraviolet irradiation from a hydrogen arc-lamp. A Pm^{147} beta-ray source, used in place of the photocathode, permitted outputs of over 5 microamperes. Figure 2 shows a typical multiplier gain curve using the Pm^{147} activating electron source. Overall multiplier gains of up to 10^5 were readily obtainable.

The gain of the multipliers, when evaluated in gain-decay studies, decreased rapidly initially, reaching a plateau where the rate of gain decay approached zero in a few hours. The output current at this plateau was still sufficient for ionization purposes. In operation, the dynode gain would be allowed to decay until the plateau region was reached, before beginning analyses; this would be analogous to conditioning a thermionic emitter, prior to use.

The lifetime of the multipliers, defined as the time required for the output current to decay to one-half its initial value, was a function of the output current level and the atmosphere in which it was operated. In an oil-diffusion pumped vacuum system, the lifetime at 1.0 microampere output was less than one-fourth that obtained when the output was 0.5 microampere. In an ion getter pumped vacuum system, the lifetime was significantly increased because of the cleanliness of the system. The multiplier output current, as a function of time, for the ion getter pumped system, is shown in Figure 3. The discontinuities occurred when the multiplier was turned off over night

and restarted the next morning. The output, as can be seen, quickly returned to the output of the previous day.

In all cases, however, the dynode resistance decreased to less than 25 percent of the original resistance. This resistance decrease was attributed to carbonaceous deposits caused by the interaction of the electron beam with surface contaminants and trapped molecules in the metal film. The resistance would stabilize out at this lower value of resistance, with little or no further decrease, after 6 to 8 hours of operation.

Although the lifetime was greatly extended when the multiplier was operated in the ion getter pumped vacuum system, the dynodes were prepared in an oil-diffusion pumped vacuum system. Thus, oil molecules were trapped on the substrate and in the film during deposition. It is not possible, therefore, to obtain a surface completely free from hydrocarbons, even when operating in a "clean" vacuum system. However, since the multiplier lifetime was directly related to the atmosphere in which it was operated, it is concluded that this device is practical, for long-term use, only when used in an ion getter pumped vacuum system.

Electron emission from this source very gradually decreases over a period of time; therefore the time constant of response of an emission regulator associated with type of source would be relatively large. Since there is no electrical connection or continuity between the ultraviolet radiation emerging from the hydrogen arc lamp to the photocathode, this particular closed-loop, feedback-control system is simplified considerably as to its electronic aspects.

One approach to emission control would involve variation in the ultraviolet radiation intensity impinging on the photocathode so as to cause the number

of electrons leaving the multiplier to remain constant. A conventional servo-motor drive, controlled by a DC signal from the ionizing electron catcher, could be used to control the current flowing through the hydrogen arc-lamp by means of an autotransformer or rheostat. Or an adjustable iris could be placed between the lamp and the sapphire window. A servo-motor mechanism to adjust the diameter of this iris could vary the intensity of the ultraviolet radiation over a wide range of values, while at the same time, the lamp current could be adjusted to a point at which the hydrogen lamp would present a stable mode of operation.

Another approach to emission regulation control involves varying the multiplier dynode voltage. Initial results indicate that the dynode voltage can be altered to some extent without affecting the electron energy distribution. Further study is indicated, however, prior to detailed consideration of this method of regulation.

These multipliers were initially evaluated as ion gauges to test their feasibility as mass spectrometric sources. They were found to possess a linear ion-current-pressure relationship to at least 1×10^{-7} torr, and to have a sensitivity slightly greater than that of the RCA 1949 or Bayard-Alpert triode ionization gauges. Typical pressure-ion current curves for the multiplier ion gauge are shown in Figure 4.

Electron energy distribution studies conducted using the multiplier ion gauges showed that the relative energy distribution of the output electrons did not change with variation of multiplier gain. A typical multiplier output electron energy distribution curve is shown in Figure 5. The fact that the electron energy distribution does not change is extremely important. A mass

spectrometric source must possess this characteristic. This requirement is necessary because a mass spectrometer depends upon its ion source to form ions in a constant manner. It is to be noted that monoenergetic electrons are not an absolute necessity for mass spectrometric use. If the electron energy distribution varies, however, the manner in which the ions are formed, i.e., the cracking pattern will vary. If the cracking pattern varies with time, analysis attempts are futile.

A multiplier, utilizing commercially prepared dynodes, was found to have inadequate electron current output for mass spectrometric applications. The dynodes, evaluated and compared with dynodes prepared by this laboratory, were found to be operationally inferior to our dynodes, both in electron current capability and lifetime. The resistance-strip multiplier, having demonstrated constant output electron energy distribution and linear pressure-ion current relationships, was installed as a cold electron bombardment ion source[3]. The mass spectrometer chosen for evaluation of the cold source was a three-stage RF mass spectrometer.

The RF mass spectrometer, as an analytical instrument, was first developed by Bennett[1]. Improvement on the original design has been made by Testerman[5,6] to provide a rugged and reliable RF mass spectrometer. An operational diagram of the cold source assembly is shown in Figure 6. The electrons, which are emitted in an almost unidirectional path from the multiplier, are directed into the ionizing region of the spectrometer by a difference potential of +100 volts (this is the ionizing potential). The ionizing region is maintained at ground potential while the dynode exit potential is at -100 volts. The ions thus formed by the electron bombardment of neutral gas

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molecules are attracted into the analyzer by the first pulling out grid of the analyzer, which is maintained at -35 volts. The grid apertures used for the ionization region and the analyzer are quite large; the grid mesh covering the apertures affording a transparency of over 95 percent. There are no slits in this ion source that would decrease the electron current from the source. The ionization efficiency of the source is therefore quite high, providing relatively large ion currents when compared to other source configurations. Thus, the multiplier source, mounted in this manner, affords maximum use of the electrons emitted from the multiplier.

The mass spectrometer was operated using this ionization source. Spectra for air at 1 x 10^{-5} torr were run and peaks produced by the characteristic fragmentation of the molecular species were obtained. These spectra were similiar to those obtained from a conventional thermionic emitter with important exceptions, as noted below. The use of the multiplier cold electron source eliminated several of the problems normally encountered when using a thermionic emitter.

The ratio of the 28 peak to the 32 peak was less than that obtained from the previous runs using a rhenium filament ionization source. This indicated that there was little or no gettering of the air sample by the multiplier; the percentage of oxygen in the spectra being higher than with spectra obtained with a thermionic emitter. No serious outgassing effects were observed when the multiplier was used for producing ionizing electrons. Since the multiplier source operated at a temperature only slightly above room temperature there would be no contribution to the mass 28 peak caused by carbon monoxide production at the source. Substitution of the multiplier source for the hot

filament definitely eliminated the possibility of reaction by the components of the gas to be analyzed; thermal-cracking of the molecules in the sample; temperature variations in the ion source; and accumulated deposits in the mass spectrometer due to evaporated metal or metal oxides from the filament and reaction products. These accumulated deposits can cause delay in the pump-down recovery time of the system, contribute to the mass spectra causing possible erroneous results, and if insulating, cause spurious potentials on control surfaces.

Initially, prior to installation of the deflection plate shown in Figure 6, the electrons exiting from the multiplier were deflected by the magnetic field of the multiplier. Because of this deflection the electrons were not entering the ionization region and no ions were formed. Addition of the deflection plate corrected this situation by effectively negating the magnetic field effect on the electrons until the electrons had moved past the end of the plate. The magnetic field intensity varied exponentially with distance from the end of the multiplier. The radius of curvature for electrons at a distance corresponding to the end of the deflection plate was about 6 cm. Electrons just exiting from the multiplier, without the deflection plate, would experience a deflection corresponding to a radius of less than 0.2 cm. The addition of the deflection plate allowed generation of about one nanoampere of total ion current at 1×10^{-5} torr using the multiplier ion source.

In conclusion, the resistance strip magnetic multiplier can be used as a cold source of electrons in a mass spectrometer. It is useful, however, only when a deflection plate is employed to "carry" the electrons out of the influence of the multiplier magnetic field.

The cold source of electrons described herein not only has application in the RF mass spectrometer; it also can be adapted to a time-of-flight or

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a magnetic mass spectrometer. Further, this type of electron source may find favorable utilization in any ion generation process where hot thermionic emitters create difficulties.

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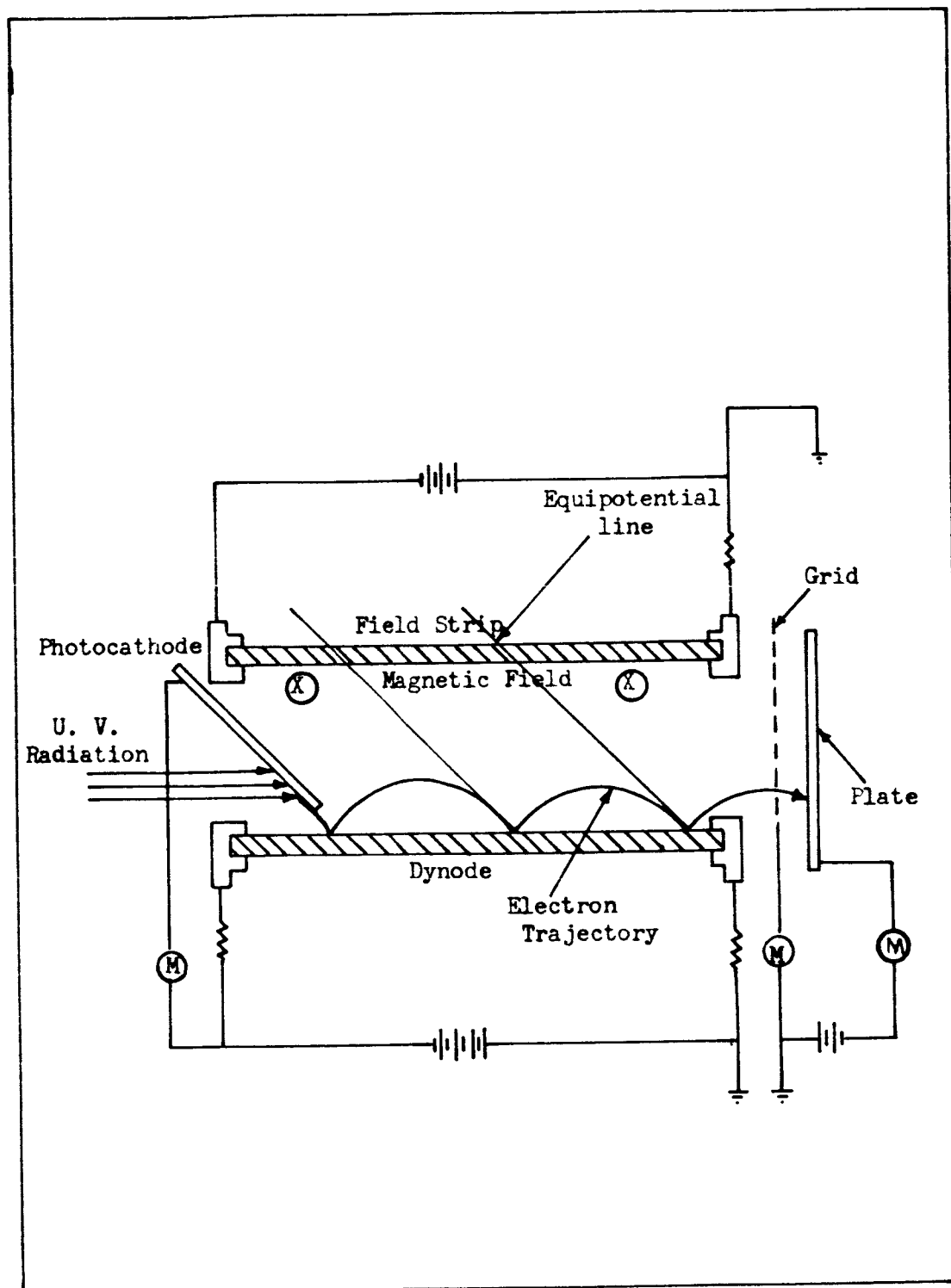
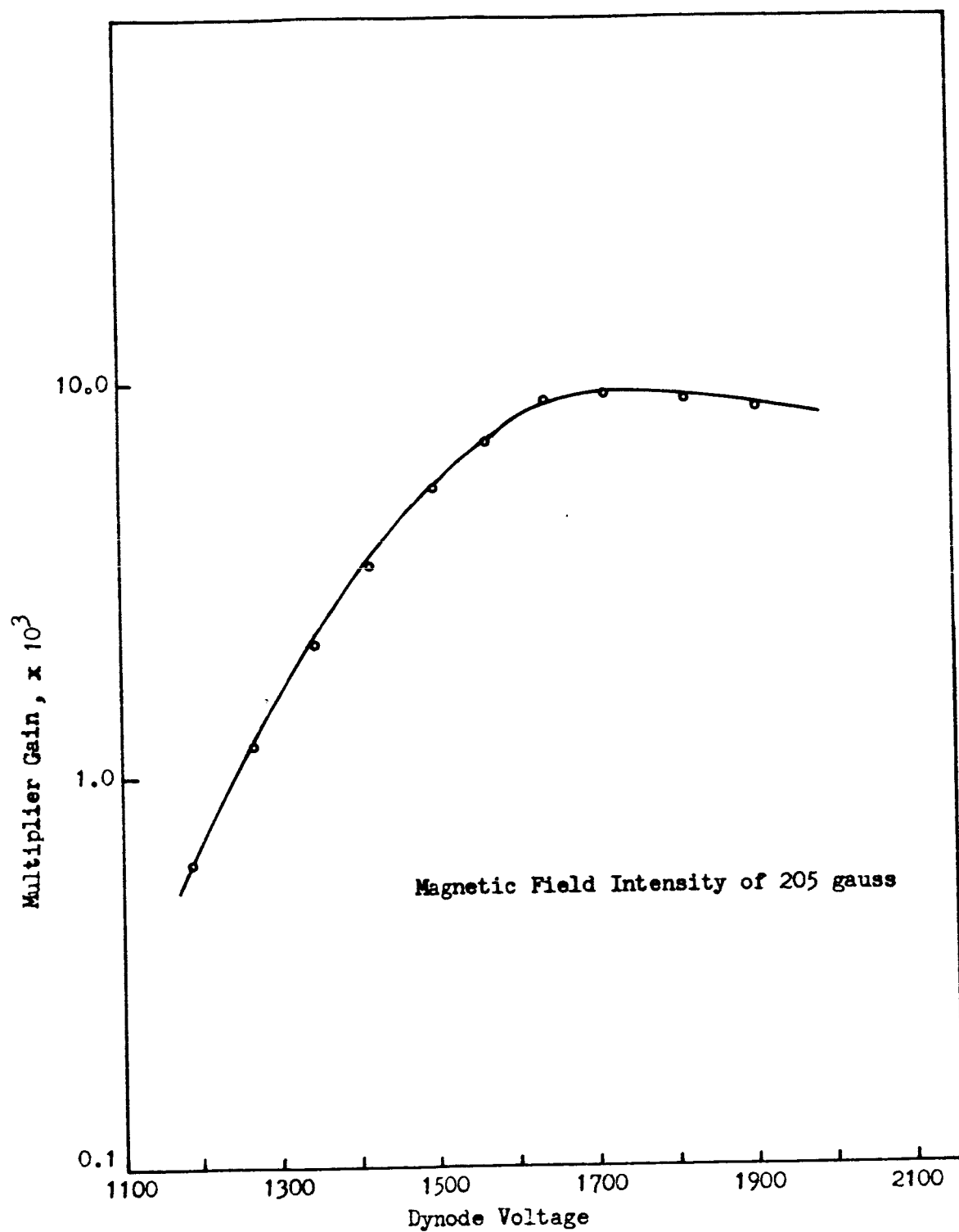Figure 1. Schematic of Resistance Strip Multiplier, as an Ion Gauge

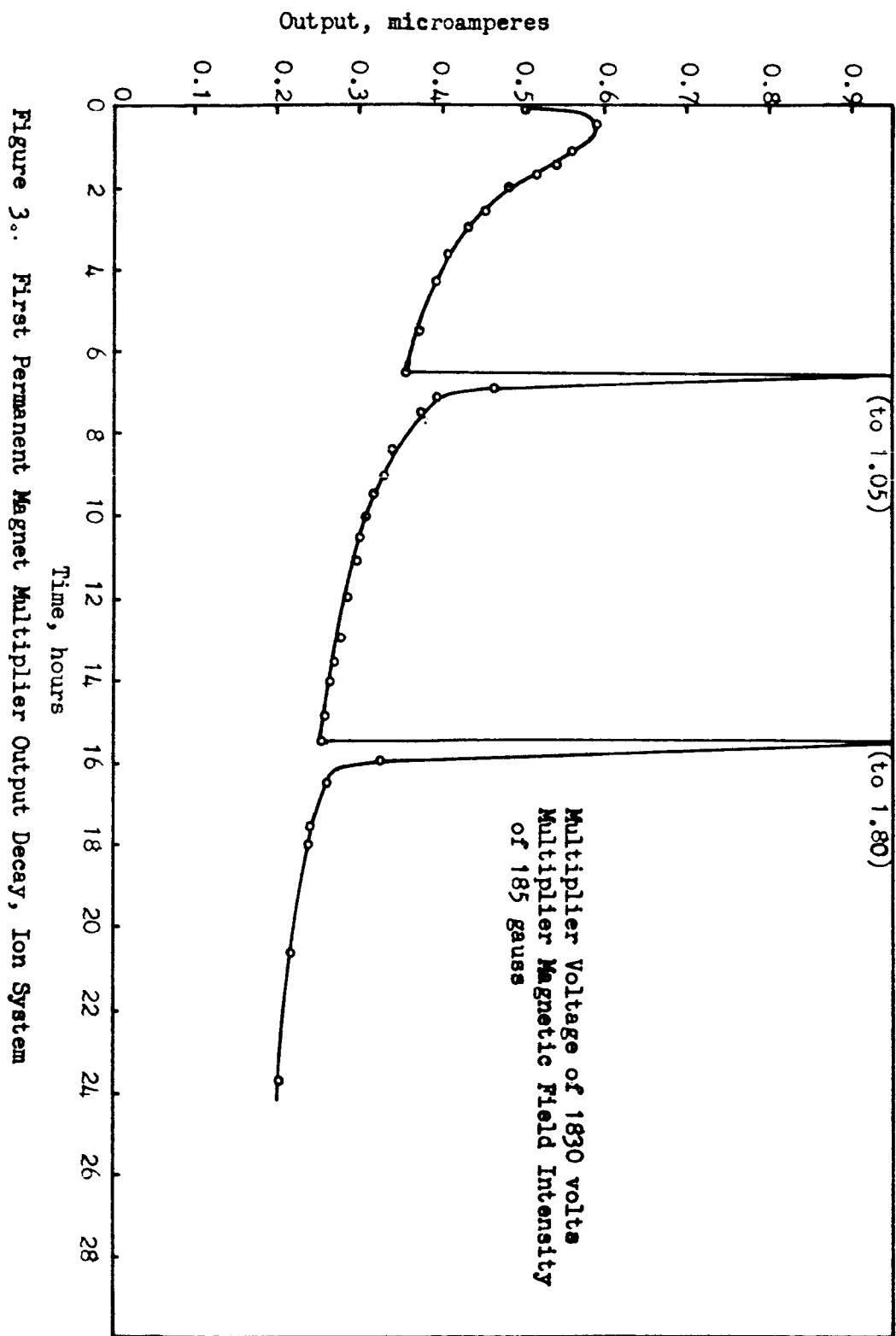Figure 2. First Permanent Magnet Multiplier Gain, Ion System

Figure 3. First Permanent Magnet Multiplier Output Decay, Ion System

Multiplier Voltage of 1830 volts
Multiplier Magnetic Field Intensity
of 185 gauss

10.0

1.0

0.1

Pressure, x 10⁻⁵ torr

(A)   (B)

(A) Grid Potential of +100 volts
(B) Grid Potential of +125 volts

Grid Current of 0.1 μA
Collector Potential of -25 volts

1.0   1.1   1.2   1.3   1.4   1.5

Log Collector Current, nanoamperes

Figure 4. Pressure Dependence of Electromagnetic Multiplier
Ion Gauge

dI/dE, nanoamperes per volt

Multiplier Voltage of 1830 volts
Multiplier Magnetic Field Intensity of 185 gauss
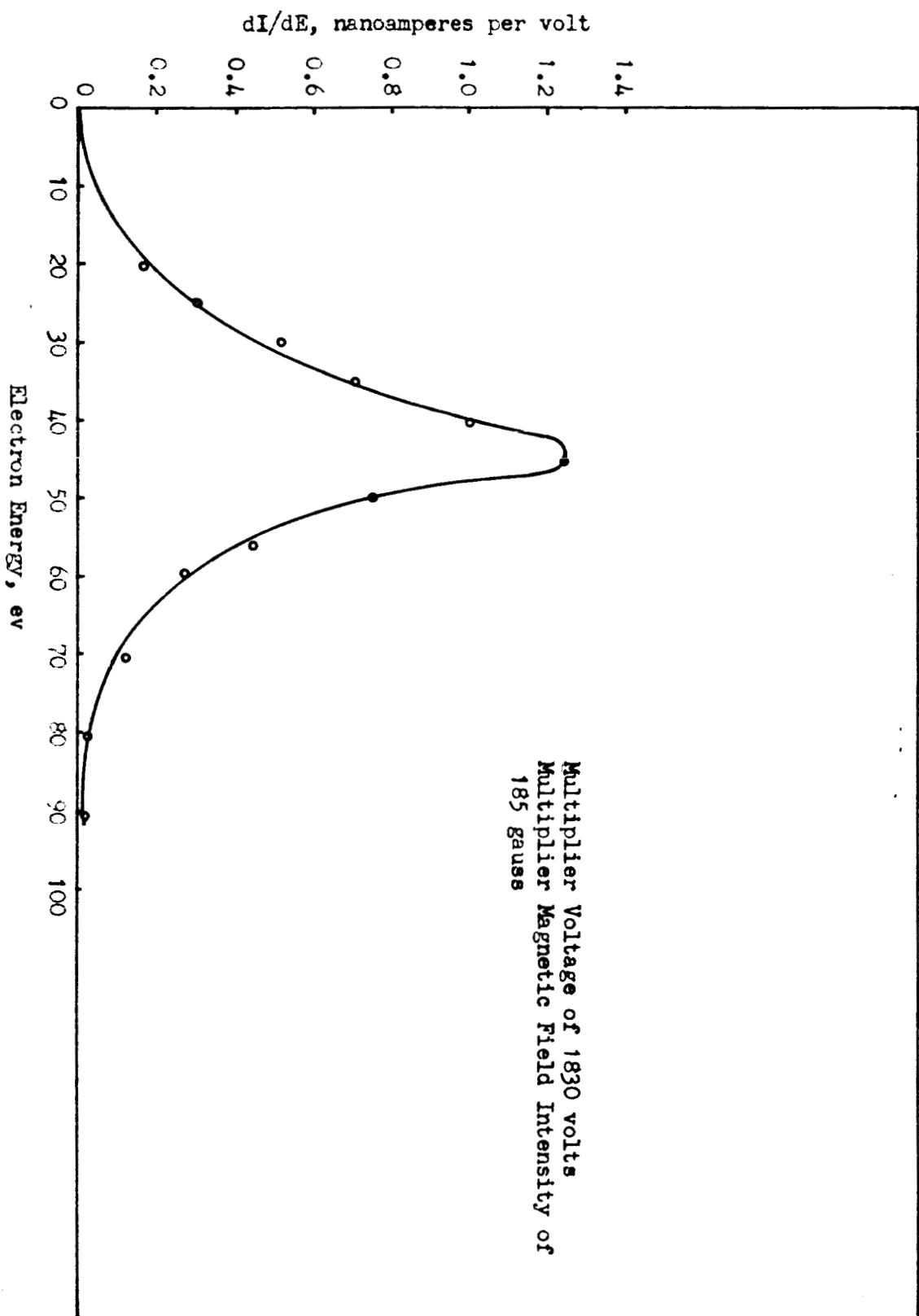
Electron Energy, ev

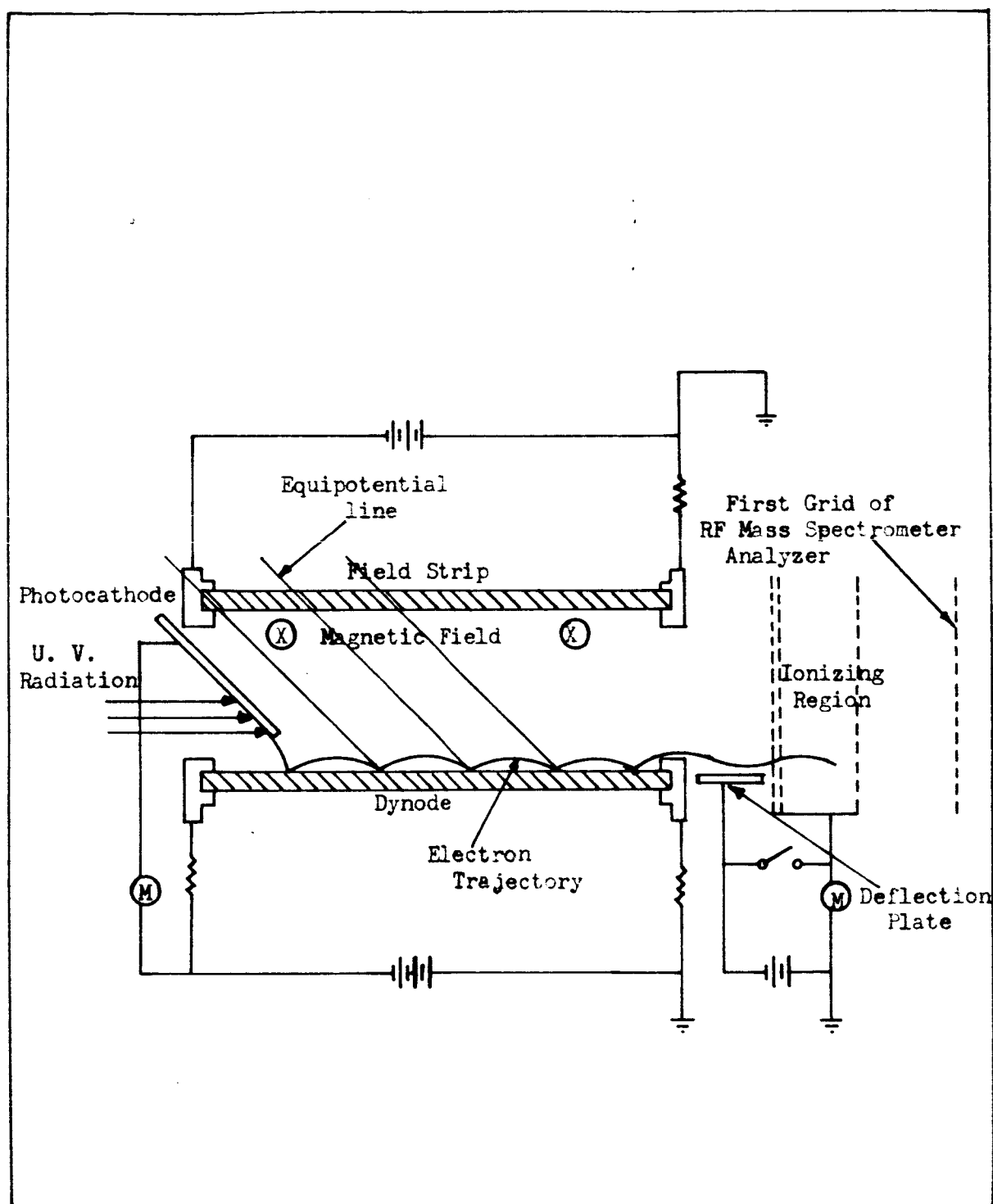Figure 5. Energy Distribution of First Permanent Magnet Multiplier Output, Ion System

Figure 6. Multiplier Assembled as Mass Spectrometric Electron
Bombardment Ion Source